PHYSICAL REVIEW VOLUME 187, NUMBER 2 10 NOVEMBER 1969

Dynamic Jahn-Teller Effect in an Orbital Triplet State Coupled to Both E_g and T_{2g} Vibrations

MARY C. M. O'BRIEN*
Mason Laboratory, Yale University, New Haven, Connecticut 06520

(Received 4 June 1969)

The Jahn-Teller coupling of a triplet state in cubic surroundings to both E_g and T_{2g} modes of vibration can lead to a vibronic ground state that includes both tetragonal and trigonal distortions if the energy difference between the static distortions is small. A simple model is set up to study the properties of this ground state, assuming the Jahn-Teller coupling is strong, so that the adiabatic approximation can be used. Expressions for the reduction factors $K(E)$ and $K(T_2)$, the g values, and their sensitivity to strains in the crystal are derived. These properties interpolate nicely between those appropriate to coupling to E_g or T_{2g} modes separately. The ground state is a triplet belonging to the same irreducible representation as the original triplet throughout the range of parameters considered.

I. INTRODUCTION

THE aim of the calculations reported here was to fill a gap in our knowledge of the properties of an orbital triplet state in a cubic environment. A full discussion and bibliography of this and other manifestations of the Jahn-Teller effect are to be found in review articles by Ham[1] and Sturge.[2] The existence of these articles makes it unnecessary to give more than a brief resume of the problem here.

Van Vleck[3] set out the problem in his classic paper on the application of the Jahn-Teller effect to paramagnetic ions in solids. When the immediate surroundings of the ion are of cubic symmetry and the ion has a triplet ground state corresponding either to a T_1 or T_2 representation of the cubic group, the ground state couples linearly to vibrations of both E_g and T_{2g} symmetry. The resulting problem, in five vibrational variables and three electronic states is complicated even if we ignore the fact that in a crystal there are many modes of each symmetry, not just one. Because of the complexity of the problem, solutions have been found only by making various assumptions about the relative values of the parameters. The important parameters are the coupling coefficients to the two sorts of normal mode and the frequencies and effective masses associated with those normal modes. Ham,[4] studying the case when the coupling is to E_g vibrations only, was able to find an exact solution for all relative values of the remaining coupling constant and the normal-mode constants. He showed that the ground state retains the same symmetry throughout, and he characterized its properties in terms of various reduced matrix elements or reduction factors. Caner and Englman[5] looked at the opposite case—coupling to T_2 vibrations only. They did the calculation numerically, also for all possible relative values of the coupling constant and the mode constants. They also found the ground state to have the same symmetry throughout, and they obtained values for the various reduction factors. If the coupling to both modes is equally important, it is more difficult to cover the whole range of coupling constants at once. If the coupling is weak, then perturbation theory can be used to find the ground state and its properties. In the present calculation we attack the case of strong coupling to both types of mode by making the extra assumptions that the coupling is about equally strong to both types of mode and that the frequencies of the modes are equal. We then take the difference in the coupling to the modes as a parameter and calculate the energy levels and ground-state reduction factors over a range of values of the parameter. It is satisfactory that the result again shows a ground state of the same symmetry throughout with reduction factors that tend towards the results of the previous calculations at the ends of the range.

TABLE I. Values of the normal coordinates at the two possible types of minima in the potential energy. The notation is Ham's[a]: The three minima of type 1 are given by taking for $e_{i\theta}$ and $e_{i\epsilon}$, the diagonal elements of ϵ_θ and ϵ_ϵ, and they correspond physically to tetragonal distortions of the cubic complex with the axis along each of the three cube axes. The four minima of type 2 correspond to trigonal distortions along the four $\langle 111\rangle$ axes, and (m_1,m_2,m_3) takes on the four sets of values $(+1, +1, +1)$, $(-1, -1, +1)$, $(+1, -1, -1)$, and $(-1, +1, -1)$. The energy at each minimum is $-E_{JT}$.

	1	2
Q_θ	$-V_E e_{i\theta}/\mu_E\omega_E^2$	0
Q_ϵ	$-V_E e_{i\epsilon}/\mu_E\omega_E^2$	0
Q_ξ	0	$(2V_T/3\mu_T\omega_T^2)m_1$
Q_η	0	$(2V_T/3\mu_T\omega_T^2)m_2$
Q_ζ	0	$(2V_T/3\mu_T\omega_T^2)m_3$
E_{JT}	$V_E^2/2\mu_E\omega_E^2$	$2V_T^2/3\mu_T\omega_T^2$

[a] Reference 1.

---

* Permanent address: Department of Theoretical Physics, Oxford University, Oxford, England.

[1] F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum Press, Inc., New York, to be published).

[2] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Vol. 20.

[3] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[4] F. S. Ham, Phys. Rev. **138**, A1727 (1965).

[5] M. Caner and R. Englman, J. Chem. Phys. **44**, 4054 (1966).

II. HAMILTONIAN AND CONDITIONS FOR THE APPEARANCE OF A DYNAMIC JAHN–TELLER EFFECT

For an orbital triplet state coupled to E_g and T_{2g} modes of vibration, the Hamiltonian can be written as

$$\mathcal{H}=V_E(Q_\theta\epsilon_\theta+Q_\epsilon\epsilon_\epsilon) +V_T(Q_\xi\tau_\xi+Q_\eta\tau_\eta+Q_\zeta\tau_\zeta)+\mathcal{H}_0\iota, \quad (2.1)$$

where

$$\mathcal{H}_0=(1/2\mu_E)[P_\theta^2+P_\epsilon^2+\mu_E^2\omega_E^2(Q_\theta^2+Q_\epsilon^2)]+(1/2\mu_T) \times[P_\xi^2+P_\eta^2+P_\zeta^2+\mu_T^2\omega_T^2(Q_\xi^2+Q_\eta^2+Q_\zeta^2)], \quad (2.2)$$

$$\epsilon_\theta=\begin{bmatrix}\frac{1}{2}&0&0\\0&\frac{1}{2}&0\\0&0&-1\end{bmatrix},\quad \epsilon_\epsilon=\begin{bmatrix}-\frac{1}{2}\sqrt{3}&0&0\\0&+\frac{1}{2}\sqrt{3}&0\\0&0&0\end{bmatrix},$$

$$\iota=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix},\quad \tau_\xi=\begin{bmatrix}0&0&0\\0&0&-1\\0&-1&0\end{bmatrix}, \quad (2.3)$$

$$\tau_\eta=\begin{bmatrix}0&0&-1\\0&0&0\\-1&0&0\end{bmatrix},\quad \tau_\zeta=\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&0\end{bmatrix}.$$

The notation used is that of Ham,[1] Q_θ and Q_ϵ are normal coordinates of the E_g mode, and Q_ξ, Q_η, and Q_ζ of the T_{2g} mode. The Hamiltonian is the same whether the orbital triplet is of T_1 or T_2 type

In the adiabatic approximation, in which the nuclear kinetic energies (all the terms in P) are neglected, the lowest eigenvalue of this Hamiltonian is a function of the Q's and can be regarded as a potential-energy function in the five-dimensional Q space. In the limit of infinitely large nuclear masses we expect the equilibrium configuration of the complex to correspond to the minimum value of this potential energy. The positions and natures of the turning points in this potential energy were discussed by Öpik and Pryce,[6] who showed that two families of minima may exist with the values of Q shown in Table I. They showed that these two types of minima do not exist in the same system: If $V_E^2/2\mu_E\omega_E^2>2V_T^2/3\mu_T\omega_T^2$, then the tetragonal distortions are minima and the trigonal distortions are saddle points, and conversely. Since in general the minima are separated from each other, the system cannot move freely from one to another without acquiring some sort of activation energy. Öpik and Pryce also identified a third set of stationary points in the energy, at $\frac{1}{4}(V_E^2/2\mu_E\omega_E^2)+\frac{3}{4}(2V_T^2/3\mu_T\omega_T^2)$; this represents the height of the saddle between two minima; that is to say, if we choose a path between two minima to minimize the maximum potential energy on that path, that maximum potential energy is the one given here.

To get dynamic Jahn-Teller effects we need paths from one minimum of V to another along which the potential-energy changes are small. It is obvious that this happens in this system if

$$V_E^2/2\mu_E\omega_E^2\approx 2V_T^2/3\mu_T\omega_T^2. \quad (2.4)$$

If these two energies are exactly equal, not only are the trigonal and tetragonal distortions and intermediate stationary points all of the same energy, but as we shall show, there exists a two-dimensional region of Q space connecting these points in which the energy remains constant. To show this, let us start by making a change of variable in the Hamiltonian: Put

$$\begin{aligned} q_\theta&=(\omega_E\sqrt{\mu_E})Q_\theta, & q_\xi&=(\omega_T\sqrt{\mu_T})Q_\xi,\\ q_\epsilon&=(\omega_E\sqrt{\mu_E})Q_\epsilon, & q_\eta&=(\omega_T\sqrt{\mu_T})Q_\eta, \quad (2.5)\\ & & q_\zeta&=(\omega_T\sqrt{\mu_T})Q_\zeta, \end{aligned}$$

so that the Hamiltonian can be written as

$$\mathcal{H}=\frac{V_E}{\omega_E\sqrt{\mu_E}}\begin{bmatrix}q_\theta-\frac{1}{2}\sqrt{3}q_\epsilon&-\lambda q_\zeta&-\lambda q_\eta\\-\lambda q_\zeta&\frac{1}{2}q_\theta+\frac{1}{2}\sqrt{3}q_\epsilon&-\lambda q_\xi\\-\lambda q_\eta&-\lambda q_\xi&-q_\theta\end{bmatrix} +\iota[\tfrac{1}{2}\omega_E^2(p_\theta^2+p_\epsilon^2)+\tfrac{1}{2}\omega_T^2(p_\xi^2+p_\eta^2+p_\zeta^2) +\tfrac{1}{2}(q_\theta^2+q_\epsilon^2+q_\xi^2+q_\eta^2+q_\zeta^2)]. \quad (2.6)$$

Here $\lambda=(V_T/\omega_T\sqrt{\mu_T})/(V_E/\omega_E\sqrt{\mu_E})$, and the condition for equal energy at the trigonal and tetragonal distortions is $\lambda^2=\frac{3}{4}$. Now it is obvious that if we neglect the kinetic energy, any linear orthogonal transformation on the q's leaves the diagonal part of the Hamiltonian invariant, so that we must look for an orthogonal transformation which leaves the roots of the matrix invariant. The required transformation is one in which the five q's taken together transform like a set of d states in the same space in which the orbital triplet basis states transform like a set of p states.

To show this, we consider the following parametrization of the q's:

$$\begin{aligned} &q_\theta=q\tfrac{1}{2}(3\cos^2\theta-1), \quad q_\epsilon=q\tfrac{1}{2}\sqrt{3}\sin^2\theta\cos 2\phi,\\ &q_\xi=q\tfrac{1}{2}\sqrt{3}\sin 2\theta\sin\phi, \quad q_\eta=q\tfrac{1}{2}\sqrt{3}\sin 2\theta\cos\phi, \quad (2.7)\\ &q_\zeta=q\tfrac{1}{2}\sqrt{3}\sin^2\theta\sin 2\phi. \end{aligned}$$

With this, if q is held constant while θ and ϕ are allowed to vary, the representative point in q space moves on a particular two-dimensional surface, which maps on the surface of a sphere in three-dimensional space. It is easily verified that with these limitations the q's satisfy

$$q_\theta^2+q_\epsilon^2+q_\xi^2+q_\eta^2+q_\zeta^2=q^2. \quad (2.8)$$

Also, the tetragonal turning points occur at

$$\begin{aligned} &q=V_E/\omega_E\sqrt{\mu_E},\\ &(\theta,\phi)=(0,0),\ (\tfrac{1}{2}\pi,0),\ (\tfrac{1}{2}\pi,\tfrac{1}{2}\pi), \quad (2.9)\\ &(\pi,0),\ (\tfrac{1}{2}\pi,\pi),\ (\tfrac{1}{2}\pi,\tfrac{3}{2}\pi), \end{aligned}$$

---

[6] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London), **A238**, 425 (1957).

and the trigonal turning points are at

$$q=(2\lambda/\sqrt{3})(V_E/\omega_E\sqrt{\mu_E}), \tag{2.10}$$
$$(\theta,\phi)=(\theta_T,\tfrac{1}{4}n\pi),\ (\pi-\theta_T,\ \tfrac{1}{4}n\pi),\quad n=1,3,5,7$$

where $\cos\theta_T=1/\sqrt{3}$. Note that in this representation, if we take the obvious limits on θ and ϕ allowing the representative point in (q,θ,ϕ) space to lie on a sphere of radius q, each real configuration of the q's appears twice, so that points related to each other by inversion in the (q,θ,ϕ) space correspond to the same point in the original q space. This will become important in determining boundary conditions, and it has the effect here of making every turning point appear twice in the above list.

We now set $\lambda=\frac{1}{2}\sqrt{3}$ and demonstrate the existence of a continuous distribution of minima in the potential energy. Suppose that initially the system is in one of its tetragonal distortions, so that $q_\theta=q$, and the other q's are zero. The matrix part of $\mathcal{H}$ is

$$\frac{V_E}{\omega_E\sqrt{\mu_E}}\begin{bmatrix}\frac{1}{2}q & 0 & 0\\ 0 & \frac{1}{2}q & 0\\ 0 & 0 & -q\end{bmatrix}, \tag{2.11}$$

which operates within a set of states we may represent by $|\xi'\rangle$, $|\eta'\rangle$, $|\zeta'\rangle$; $|\zeta'\rangle$ being the lowest eigenstate. We now make an orthogonal transformation on the basis states in the following form:

$$\begin{bmatrix}\xi'\\ \eta'\\ \zeta'\end{bmatrix}=\begin{bmatrix}\cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta\\ -\sin\phi & \cos\phi & 0\\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta\end{bmatrix}\times\begin{bmatrix}\xi\\ \eta\\ \zeta\end{bmatrix}. \tag{2.12}$$

This represents a rotation in (q,θ,ϕ) space. It is not a general one since it has been made to depend on only two angles, not three, but it is sufficiently general for this purpose. It has been chosen so that $|\zeta'\rangle$, which we know is the lowest eigenvector, is given by

$$\sin\theta\cos\phi|\xi\rangle+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle. \tag{2.13}$$

If we use this matrix and its inverse to transform the Hamiltonian so that it operates in the states $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ a little matrix multiplication gives

$$\mathcal{H}'=\frac{V_E}{\omega_E\sqrt{\mu_E}}\begin{bmatrix}\frac{1}{2}q_\theta-\frac{1}{2}\sqrt{3}q_\epsilon & -\frac{1}{2}\sqrt{3}q_\zeta & -\frac{1}{2}\sqrt{3}q_\eta\\ -\frac{1}{2}\sqrt{3}q_\zeta & \frac{1}{2}q_\theta+\frac{1}{2}\sqrt{3}q_\epsilon & -\frac{1}{2}\sqrt{3}q_\xi\\ -\frac{1}{2}\sqrt{3}q_\eta & -\frac{1}{2}\sqrt{3}q_\xi & -q_\theta\end{bmatrix}, \tag{2.14}$$

if the q's are as given in Eq. (2.7). The diagonal part of the potential energy, unaltered by the transformation, remains equal to $\frac{1}{2}q^2$. We may thus deduce that if the q's are restricted to the values given by (2.7), then the lowest eigenvalue of the Hamiltonian (2.14) is at $-qV_E/\omega_E\sqrt{\mu_E}$, and its appropriate eigenvector is

$$\sin\theta\cos\phi|\xi\rangle+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle. \tag{2.15}$$

Including the term $\frac{1}{2}q^2$ in the Hamiltonian, and minimizing with respect to q, gives $q=V_E/\omega_E\sqrt{\mu_E}$, and $E=-\frac{1}{2}V_E^2/\mu_E\omega_E^2$ for the equipotential surface of lowest potential energy.

This has demonstrated that if $\lambda=\frac{1}{2}\sqrt{3}$, there is a continuous two-dimensional distribution of minima in the potential energy, with the q's given by (2.7). If $\lambda=-\frac{1}{2}\sqrt{3}$, all the arithmetic can be done in the same way if we start by putting $q_\xi=-(\omega_T\sqrt{\mu_T})Q_\xi$ and so on. Although the actual physical shape of the distorted complex will be quite different in this case, much of the theory that follows will be done in exactly the same way. To satisfy ourselves that the continuum of minima is no more than two-dimensional, we look again at the Hamiltonian (2.11), and introduce the Hamiltonian (2.6) as a perturbation. Working to second order in the perturbation, the energy of the ground state is seen to be

$$-q\frac{V_E}{\omega_E\sqrt{\mu_E}}-\delta q_\theta\frac{V_E}{\omega_E\sqrt{\mu_E}}-\lambda^2\frac{(\delta q_\eta{}^2+\delta q_\xi{}^2)}{\frac{3}{2}q}\frac{V_E}{\omega_E\sqrt{\mu_E}}$$
$$+\tfrac{1}{2}[(q+\delta q_\theta)^2+\delta q_\epsilon{}^2+\delta q_\xi{}^2+\delta q_\eta{}^2+\delta q_\zeta{}^2] \tag{2.16}$$

and setting $q=V_E/\omega_E\sqrt{\mu_E}$ and $\lambda^2=\frac{3}{4}$ makes this

$$-\tfrac{1}{2}q^2+\tfrac{1}{2}(\delta q_\theta{}^2+\delta q_\epsilon{}^2+\delta q_\zeta{}^2), \tag{2.17}$$

from which it is clear that only two of the parameters $q_\theta\cdots q_\zeta$ can be altered without increasing the potential energy, and that the curvatures of V associated with changes in the other three are equal, and equal to one in these units. It is also clear that this state of affairs will hold at all points on this two-dimensional surface, since the transformation (2.12) takes this special point into all the others.

Now, what about the kinetic energy? This is obviously invariant under these same transformations if $\omega_E=\omega_T$. We assume this equality holds and explore the consequences. We need to find the transformation on $\sum p^2$, or the Laplacian, that is equivalent to the transformation (2.7) on the q's. Since we have not specified a complete transformation of the five q's in terms of five new variables, we cannot get a complete expression for the transformed Laplacian, but by making some assumptions we can find the part of it which depends on θ and ϕ. It is necessary to assume that the transformation is orthogonal and that the coefficients of the suppressed variables in the metric tensor are independent of θ and ϕ. It is easy enough to ensure that this is so in the neighborhood of any point on the sphere in (q,θ,ϕ) space, and since we are interested in motion on this sphere, that should suffice. The line element, for variations in θ and ϕ alone, is easily found to be

$$ds^2=dq_\theta{}^2+dq_\epsilon{}^2+dq_\xi{}^2+dq_\eta{}^2+dq_\zeta{}^2$$
$$=3q^2d\theta^2+3q^2\sin^2\theta d\phi^2, \tag{2.18}$$

which leads to an expression for the Laplacian,

$$\frac{1}{3q^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{3q^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}, \qquad (2.19)$$

so that in the kinetic-energy part of the Hamiltonian (2.6) we can set

$$\frac{\partial^2}{\partial q_\theta^2}+\frac{\partial^2}{\partial q_\epsilon^2}+\frac{\partial^2}{\partial q_\xi^2}+\frac{\partial^2}{\partial q_\eta^2}+\frac{\partial^2}{\partial q_\zeta^2}$$

$$=\frac{1}{3q^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \qquad (2.20)$$

and the kinetic energy becomes

$$-\iota\frac{1}{2}\frac{\hbar^2\omega^2}{3q^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \qquad (2.21)$$

Now we assume that the increase in potential energy as we leave this equipotential surface is so sharp that such excursions can be neglected and solve the Schrödinger equation in the remaining variables, θ and ϕ. This Schrödinger equation has a constant potential energy, which we shall omit, and simply takes the form

$$-\frac{\hbar^2\omega^2}{6q^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi=E\psi, \qquad (2.22)$$

which is, of course, just the same as the equation for the square of the total angular momentum of a spherically symmetric system. The eigenvalues are

$$(\hbar^2\omega^2/6q^2)l(l+1), \qquad (2.23)$$

where l is an integer under the usual boundary conditions.

To find the appropriate boundary conditions for this system, we must go back to the wave function (2.15) and realize that the complete vibronic eigenstate must have the form

$$\psi(\theta,\phi)(\sin\theta\cos\phi|\xi\rangle+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle). \qquad (2.24)$$

Now under inversion in (q,θ,ϕ) space the electronic wave function changes sign, while the q's remain unaltered. This operation of inversion, which does nothing physically to the system, must not alter the total wave function, so $\psi(\theta,\phi)$ must change sign under inversion. This means that the eigenstates must be limited to those corresponding to odd values of l, and that in particular the lowest energy level is a vibronic triplet corresponding to $l=1$.

Now we can look at one criterion for the validity of this approximation. We have found that the spacing of energy levels associated with motion on the minimum potential energy sphere in (q,θ,ϕ) space is of the order of $\hbar^2\omega^2/q^2$. For motion orthogonal to this surface the potential is harmonic, with the restoring force associated with the frequency ω. Hence, the characteristic separation of energy levels for this type of motion is $\hbar\omega$. Consequently, we may look at motion on the spherical surface on its own as long as the energies concerned are very much less than $\hbar\omega$, that is, as long as

$$\hbar^2\omega^2/q^2\ll\hbar\omega \qquad (2.25)$$

or

$$E_{JT}\gg\tfrac{1}{2}\hbar\omega. \qquad (2.26)$$

Here we have used $E_{JT}=V_E^2/2\mu_E\omega^2=\frac{1}{2}q^2$, so that for the vibronic spacing parameter, we have $\hbar^2\omega^2/q^2=\hbar^2\omega^2/2E_{JT}$.

The properties of such a dynamic Jahn-Teller ground state can be expressed in terms of a set of reduction factors used by Ham[4] and by Caner and Englman.[5] These relate the effect of an operator of any symmetry within the original three orbital states to its effect within the actual triplet ground state. Of these three reduction factors $K(T_1)$ is identically zero in this approximation, since it relates to an operator such as orbital angular momentum whose expectation value is zero in a real orbital singlet state, which is what our orbital state is. The other two reduction factors $K(E)$ and $K(T_2)$ can be found in Ref. 1, Eq. (3.1.10):

$$K(E)=-\langle\psi_{g\zeta}|\epsilon_\theta|\psi_{g\zeta}\rangle, \quad K(T_2)=-\langle\psi_{g\xi}|\tau_\zeta|\psi_{g\eta}\rangle. \qquad (2.27)$$

We have not yet identified the three components of the ground-state wave function, so we can choose

$$\begin{aligned}\psi_{g\xi}&=(\tfrac{3}{4}\pi)^{1/2}\sin\theta\cos\phi(\sin\theta\cos\phi|\xi\rangle\\&\qquad+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle),\\ \psi_{g\eta}&=(\tfrac{3}{4}\pi)^{1/2}\sin\theta\sin\phi(\sin\theta\cos\phi|\xi\rangle\\&\qquad+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle), \qquad (2.28)\\ \psi_{g\zeta}&=(\tfrac{3}{4}\pi)^{1/2}\cos\theta(\sin\theta\cos\phi|\xi\rangle\\&\qquad+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle),\end{aligned}$$

which have been normalized over the surface of a unit sphere in (q,θ,ϕ) space. Then

$$\langle\psi_{g\zeta}|\epsilon_\theta|\psi_{g\zeta}\rangle=\frac{3}{4\pi}\int\int\cos^2\theta(-\cos^2\theta+\tfrac{1}{2}\sin^2\theta\cos^2\phi$$
$$+\tfrac{1}{2}\sin^2\theta\sin^2\phi)\sin\theta d\theta d\phi=-\tfrac{2}{5},$$

so that $K(E)=+\frac{2}{5}$, and

$$\langle\psi_{g\xi}|\tau_\zeta|\psi_{g\eta}\rangle$$
$$=\frac{3}{4\pi}\int\int\sin^2\theta\cos\phi\sin\phi(-2\sin^2\theta\cos\phi\sin\phi)$$
$$\times\sin\theta d\theta d\phi=-\tfrac{2}{5},$$

so that $K(T)=+\frac{2}{5}$ also.

III. EIGENVALUE PROBLEM WHEN TRIGONAL AND TETRAGONAL ENERGIES ARE DIFFERENT

As soon as $\lambda^2-\frac{3}{4}$ becomes different from zero, the rotational symmetry of the equipotential surface in (q,θ,ϕ) space is lost. We are faced with the problem of finding the lowest root of a cubic equation, and then using that lowest root as the potential energy for the nuclear Schrödinger equation. Even when $\lambda^2-\frac{3}{4}$ is small we have not got an analytic expression for the lowest root of the cubic equation, and hence do not know the form of the potential energy as a function of the q's. However, it is reasonable to assume that there is no drastic change in the potential energy as $\lambda^2-\frac{3}{4}$ becomes different from zero, and that as long as the difference between the energies of the trigonal and tetragonal distortions is small compared with the total Jahn-Teller energy, the potential energy on our sphere in (q,θ,ϕ) space is still much lower than anywhere else, though it is no longer constant.

What we shall do then is to continue to assume that the system is constrained to move on the (q,θ,ϕ) sphere, and we shall add to the Hamiltonian a term $V(\theta,\phi)$ to represent differences of potential on that surface. Now we know that $V(\theta,\phi)$ must have either maxima or minima at the tetragonal points, and either minima or maxima at the trigonal turning points; it must also have saddle points at the intermediate turning points, which in (q,θ,ϕ) space occur at

$$(\theta,\phi)=(\tfrac{1}{4}\pi,\tfrac{1}{2}n\pi),\ (\tfrac{3}{4}\pi,\tfrac{1}{2}n\pi),\ (\tfrac{1}{2}\pi,\ \tfrac{1}{4}\pi+\tfrac{1}{2}n\pi),\quad n=0,\,1,\,2,\,3. \tag{3.1}$$

In Fig. 1 a contour map is sketched on a spherical surface to show the main characteristics of $V(\theta,\phi)$.

The simplest form of $V(\theta,\phi)$ that we can write down satisfying these conditions is the combination of fourth-order spherical harmonics that has cubic symmetry, the usual fourth-order cubic field term,

$$V(\theta,\phi)=\Delta\{Y_4{}^0(\theta,\phi)+(5/14)^{1/2}[Y_4{}^4(\theta,\phi)+Y_4{}^{-4}(\theta,\phi)]\}, \tag{3.2}$$

which can also be expressed in Cartesians as

$$(x^4+y^4+z^4-\tfrac{3}{5}r^4)_{r=\text{const}}, \tag{3.3}$$

and it is easy to show that the turning points in it are as required. If the parameter Δ is positive it is the trigonal distortions which are the minima of V, while if Δ is negative it is the tetragonal distortions. Now the Schrödinger equation to be solved is

$$-\frac{\hbar^2\omega^2}{6q^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi+V(\theta,\phi)\psi=E\psi. \tag{3.4}$$

Since this is in any case only an approximation that is expected to hold when V is small, we can start from the eigenstates of the equation with $V=0$, calculate the matrix of V operating within the n lowest eigenstates, and diagonalize the resulting $n\times n$ matrix. This procedure has the additional advantage that the basic states are angular momentum eigenstates, and since V is expressed in spherical harmonics, all the matrix elements can be expressed in terms of $3j$ symbols, which are well known and easily manipulated. The result of such a calculation is shown in Fig. 2. For this calculation the basic states were taken up to $l=13$, and the diagram shows energy levels originating from states up to $l=7$, which should be relatively free from the effects of the cutoff at $l=13$. The range of values of Δ was chosen to be wide enough to show the lower-energy levels settling into a harmonic-oscillator pattern in the trigonal and tetragonal wells for large positive and negative values of Δ. It should be noted that a T_1 state is lowest throughout the whole range of values of Δ, which is consistent with the fact that a T_1 state is already known to be lowest when the coupling is to either the E_g or T_{2g} vibrations alone. (The labeling on the diagram corresponds to the case when the original orbital triplet is T_1. If it were T_2, the suffixes 1 and 2 should be interchanged on all T's and A's on the diagram.[7])

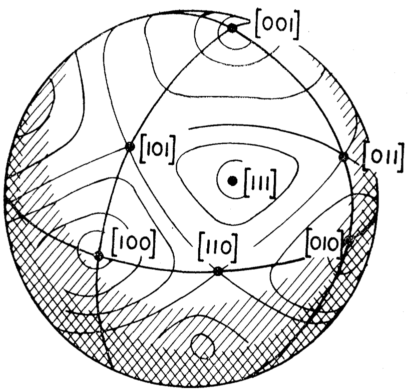

FIG. 1. Contour plot of $V(\theta,\phi)$ on a spherical surface. Tetragonal distortions are represented by all the [100] directions and trigonal distortions by all the [111] directions.

The reduction coefficients $K(E)$ and $K(T_2)$ in the ground state are easily found from the following considerations: We can write the ground-state wave functions in the form

$$\begin{aligned}\psi_{g\xi}&=f_\xi(\theta,\phi)(\sin\theta\cos\phi|\xi\rangle+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle),\\ \psi_{g\eta}&=f_\eta(\theta,\phi)(\sin\theta\cos\phi|\xi\rangle+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle),\\ \psi_{g\zeta}&=f_\zeta(\theta,\phi)(\sin\theta\cos\phi|\xi\rangle+\sin\theta\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle),\end{aligned} \tag{3.5}$$

where the functions $f_i(\theta,\phi)$ are available in the form of linear combinations of angular momentum eigenfunctions. Then

$$\langle\psi_{g\zeta}|\epsilon_\theta|\psi_{g\zeta}\rangle=\int\!\!\int f_\zeta(\theta,\phi)^2(\tfrac{1}{2}-\tfrac{3}{2}\cos^2\theta)\sin\theta d\theta d\phi \tag{3.6}$$

---

[7] Solutions of Eq. (3.4) have also been given by A. F. Devonshire, Proc. Roy. Soc. (London) **153**, 601 (1936); P. Sauer, Z. Physik **194**, 360 (1966).

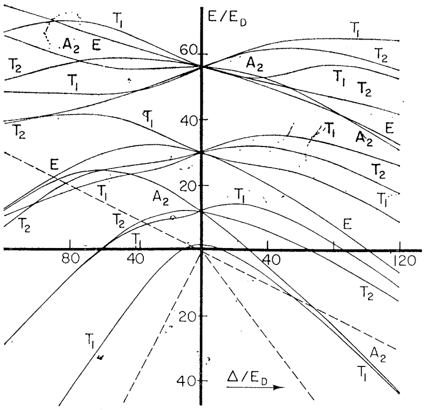

FIG. 2. Eigenvalues of Eq. (3.4). Energy is plotted in units of $E_D=\hbar^2\omega^2/6q^2$ against Δ/E_D. The dashed lines show the energies of the bottom of the potential minima and of the saddle points.

and

$$\langle\psi_{a\xi}|\tau_\zeta|\psi_{a\eta}\rangle=\int\int f_\xi(\theta,\phi)f_\eta(\theta,\phi)$$
$$\times(-2\sin^2\theta\cos\phi\sin\phi)\sin\theta d\theta d\phi, \quad (3.7)$$

from which it is clear that

$$K(E)=\langle f_\zeta|Y_2^0|f_\zeta\rangle \quad (3.8)$$

and

$$K(T_2)=\langle f_\xi|(i/\sqrt{2})(Y_2^{-2}-Y_2^2)|f_\eta\rangle. \quad (3.9)$$

These expressions are easily calculated by means of $3j$ symbols. The results of this calculation are shown in Fig. 3, where $K(E)$ and $K(T_2)$ are plotted against

$$\Delta\bigg/\left(\frac{\hbar^2\omega^2}{6q^2}\right).$$

The main point to notice from these plots is that $K(E)$ and $K(T_2)$ change rather rapidly from their value of $\frac{2}{5}$ when $\Delta=0$ and get quite close to the values appropriate to pure trigonal or tetragonal distortions, even when Δ is not particularly large. Since the results of experiment on such a system will frequently depend mainly on $K(E)$ or $K(T_2)$ this suggests that we may deduce from experiments that the system is in a state of trigonal or tetragonal distortion, even when the energy balance between the two types of distortion is not very uneven.

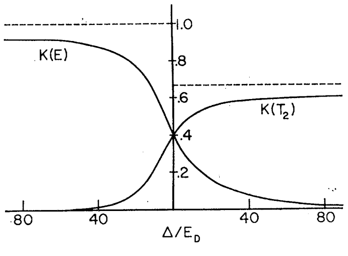

FIG. 3. $K(E)$ and $K(T_2)$ plotted against Δ/E_D.

The "cubic-field" perturbation used here will also cover the possibility that $\omega_E\neq\omega_T$, as long as the difference is not too large. If we take the Hamiltonian (2.6) and do a canonical transformation on the variables, we can put it in the form

$$H=\frac{V_E}{\omega\sqrt{\mu_E}}\begin{bmatrix}\frac{1}{2}q_\theta-\frac{1}{2}\sqrt{3}q_\epsilon & -\lambda'q_\zeta & -\lambda'q_\eta\\ -\lambda'q_\zeta & \frac{1}{2}q_\theta+\frac{1}{2}\sqrt{3}q_\epsilon & -\lambda'q_\xi\\ -\lambda'q_\eta & -\lambda'q_\xi & -q_\theta\end{bmatrix}$$
$$+\iota\{\tfrac{1}{2}\omega^2(p_\theta^2+p_\epsilon^2+p_\xi^2+p_\eta^2+p_\zeta^2)$$
$$+\tfrac{1}{2}(q_\theta^2+q_\epsilon^2+q_\xi^2+q_\eta^2+q_\zeta^2)$$
$$+[(\omega_E^2-\omega_T^2)/4\omega^2](q_\theta^2+q_\epsilon^2-q_\xi^2-q_\eta^2-q_\zeta^2)\}, \quad (3.10)$$

where $\lambda'=\lambda\omega_E/\omega_T$ and $\omega^2=\frac{1}{2}(\omega_E^2+\omega_T^2)$. This has the same form as (2.6) with $\omega_E=\omega_T$, except for the term in $(q_\theta^2+q_\epsilon^2-q_\xi^2-q_\eta^2-q_\zeta^2)$. It is easy to see by making the substitutions (2.7) that this is another cubic-field term with exactly the same angular variation as $V(\theta,\phi)$. The magnitude of this effect is best expressed as the energy difference between the maxima and minima of this extra potential energy on the $q=$ constant surface, which is just

$$[(\omega_E^2-\omega_T^2)/2\omega^2]q^2=[(\omega_E^2-\omega_T^2)/\omega^2]E_{JT}. \quad (3.11)$$

The sign increases the energy of the tetragonal distortions if $\omega_E^2>\omega_T^2$, and conversely (which is what should be expected): increasing ω_E^2 in (2.6) decreases the effective mass for vibrations near the tetragonal points, which in turn increases the zero-point energy and effectively raises the energy of the ground state above the potential energy. Thus, having $\omega_E^2>\omega_T^2$ would tend to tip the system towards the trigonal distortions relative to what would be expected from looking at the Jahn-Teller energies alone.

In summary, this transformation of the Hamiltonian shows that, as long as we are in the region in which perturbation theory can be used, making $\omega_E\neq\omega_T$ will not have any effect that is qualitatively different from having $\lambda^2\neq\frac{3}{4}$.

IV. EFFECT OF STRAIN

The effect of strains in the surroundings of the paramagnetic center can be written in terms of a Hamiltonian analagous to (2.1) as

$$\mathcal{H}_S=V_E{}^S(e_\theta\epsilon_\theta+e_\epsilon\epsilon_\epsilon)$$
$$+V_T{}^S(e_\xi\tau_\xi+e_\eta\tau_\eta+e_\zeta\tau_\zeta)+V_A{}^Se_0\iota, \quad (4.1)$$

where

$$e_\theta=e_{zz}-\tfrac{1}{2}(e_{xx}+e_{yy}),\quad e_\epsilon=\tfrac{1}{2}\sqrt{3}(e_{xx}-e_{yy}),$$
$$e_\xi=e_{yz},\quad e_\eta=e_{zx},\quad e_\zeta=e_{xy}, \quad (4.2)$$
$$e_0=e_{xx}+e_{yy}+e_{zz},\quad \text{and}\quad e_{ij}=\tfrac{1}{2}(\partial u_i/\partial x_j+\partial u_j/\partial x_i)$$

is a component of the strain tensor.[1] This will apply whether the strain is caused by local impurities in the lattice or by forces applied externally on the whole crystal. If the effects of strains are the result of movements of atoms in the immediate complex only, then $V_E{}^S$ and $V_T{}^S$ can be directly related to V_E and V_T. This will not be true in general, but it may be a good first approximation. The final term in (4.1) represents the effect of a totally symmetric strain, which alters the energies of all three states equally.

The first-order effect of this Hamiltonian in the ground triplet can be immediately written down in terms of $K(E)$ and $K(T_2)$. We simply get

$$\begin{aligned}\mathcal{H}_S={}&V_E{}^SK(E)(e_\theta\epsilon_\theta+e_\epsilon\epsilon_\epsilon)\\&+V_T{}^SK(T_2)(e_\xi\tau_\xi+e_\eta\tau_\eta+e_\zeta\tau_\zeta)+V_A{}^Se_0\iota.\end{aligned}\tag{4.3}$$

It also may be necessary to consider the effect of strains in altering the ground state by mixing in excited vibronic states. This can be done with the introduction of more parameters, though the validity of the model used here is more questionable for the excited states than for the ground state.

Let us consider, as an example, the effect of an axial strain e_θ which reduces the over-all symmetry at the site from cubic to tetragonal. Since e_θ is a member of the E representation of the cubic group, it couples the ground T_1 state to excited T_1 and T_2 triplets. We have already seen how matrix elements of the form $\langle T_1|E|T_1\rangle$ can be expressed in terms of a reduced matrix element $K(E)$, and we must now expand the notation to make it more explicit which states are concerned. We shall write the reduced matrix element between the two lowest T_1 states as $(0T_1\|E\|1T_1)$, and between T_1 and T_2 as $(0T_1\|E\|0T_2)$; in this notation $K(E)$ is $(0T_1\|E\|0T_1)$. The appropriate matrices from which we can find the admixture coefficients are then

$$V_E{}^Se_\theta(0T_1\|E\|1T_1)\epsilon_\theta\tag{4.4}$$

for the T_1 excited states, and

$$V_E{}^Se_\theta(0T_1\|E\|0T_2)\epsilon_\epsilon\tag{4.5}$$

for the T_2 excited states. The second of these two matrices is obtained by looking up coupling coefficients (for instance, in Koster *et al.*[8]), and noticing that with the obvious identification of the three components of T_2, we can use ϵ_ϵ and $-\epsilon_\theta$ for the matrices of θ and ϵ operators, respectively.

Using these matrices, we immediately find that the ground states with first-order admixtures from the lowest excited states become

$$\begin{aligned}&|0T_1\xi\rangle-\tfrac{1}{2}\mu e_\theta|1T_1\xi\rangle+\tfrac{1}{2}\sqrt{3}\mu^{\mathrm{i}}e_\theta|0T_2\xi\rangle,\\&|0T_1\eta\rangle-\tfrac{1}{2}\mu e_\theta|1T_1\eta\rangle-\tfrac{1}{2}\sqrt{3}\mu^{\mathrm{i}}e_\theta|0T_2\eta\rangle,\\&|0T_1\zeta\rangle+\mu e_\theta|1T_1\zeta\rangle,\end{aligned}\tag{4.6}$$

where

$$\begin{aligned}\mu&=V_E{}^S(0T_1\|E\|1T_1)/E(1T_1),\\\mu^{\mathrm{i}}&=V_E{}^S(0T_1\|E\|0T_2)/E(0T_2),\end{aligned}\tag{4.7}$$

and $E(1T_1)$ and $E(0T_2)$ are the excitation energies of the states above the ground state. Obviously, in general there will be coupling to many excited states, but considering one state of each symmetry should make clear the kinds of things that can happen. These reduced matrix elements can be calculated for any set of eigenstates, and in particular we have, when $\Delta=0$,

$$\begin{aligned}(0T_1\|E\|1T_1)&=3\sqrt{3}/5\sqrt{7}\approx0.39,\\(0T_1\|E\|0T_2)&=\sqrt{3}/\sqrt{35}\approx0.29.\end{aligned}\tag{4.8}$$

Since squeezing the crystal in various ways will produce more complicated strains than the simple e_θ type considered above, it will be helpful to work in a more compact notation. This is suggested by looking at the states (4.6), which can obviously be rewritten in the matrix form

$$|0T_1\rangle-\mu e_\theta\epsilon_\theta|1T_1\rangle-\mu^{\mathrm{i}}e_\theta\epsilon_\epsilon|0T_2\rangle.\tag{4.9}$$

Including the effect of an e_ϵ strain alters this to

$$|0T_1\rangle-\mu(e_\theta\epsilon_\theta+e_\epsilon\epsilon_\epsilon)|1T_1\rangle-\mu^{\mathrm{i}}(e_\theta\epsilon_\epsilon-e_\epsilon\epsilon_\theta)|0T_2\rangle.\tag{4.10}$$

Now we must include the effects of T_2-type strains; these will mix in to the ground-state symmetry states T_1, T_2, E, and A_2. Further inspection of tables of coupling coefficients shows that these admixtures can be represented in matrix form as

$$\begin{aligned}&-\mu^{\mathrm{ii}}(e_\xi\tau_\xi+e_\eta\tau_\eta+e_\zeta\tau_\zeta)|1T_1\rangle\\&\qquad-\mu^{\mathrm{iii}}(e_\xi\gamma_\xi+e_\eta\gamma_\eta+e_\zeta\gamma_\zeta)|0T_2\rangle\\&-\mu^{\mathrm{iv}}(e_\xi\alpha_\xi+e_\eta\alpha_\eta+e_\zeta\alpha_\zeta)|0A_2\rangle\\&\qquad-\mu^{\mathrm{v}}(e_\xi\beta_\xi+e_\eta\beta_\eta+e_\zeta\beta_\zeta)|0E\rangle,\end{aligned}\tag{4.11}$$

where τ_ξ, τ_η, and τ_ζ have already been defined, and

$$\begin{aligned}&\gamma_\xi=\begin{bmatrix}0&0&0\\0&0&-1\\0&1&0\end{bmatrix},\quad\gamma_\eta=\begin{bmatrix}0&0&1\\0&0&0\\-1&0&0\end{bmatrix},\quad\gamma_\zeta=\begin{bmatrix}0&-1&0\\1&0&0\\0&0&0\end{bmatrix},\\&\alpha_\xi=\begin{bmatrix}1\\0\\0\end{bmatrix},\quad\alpha_\eta=\begin{bmatrix}0\\1\\0\end{bmatrix},\quad\alpha_\zeta=\begin{bmatrix}0\\0\\1\end{bmatrix},\\&\beta_\xi=\begin{bmatrix}-\tfrac{1}{2}\sqrt{3}&-\tfrac{1}{2}\\0&0\\0&0\end{bmatrix},\quad\beta_\eta=\begin{bmatrix}0&0\\\tfrac{1}{2}\sqrt{3}&-\tfrac{1}{2}\\0&0\end{bmatrix},\quad\beta_\zeta=\begin{bmatrix}0&0\\0&0\\0&1\end{bmatrix}.\end{aligned}\tag{4.12}$$

---

[8] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the 32 Point Groups* (MIT Press, Inc., Cambridge, Mass. 1966).

$|0A_2\rangle$ represents the singlet state of symmetry A_2, while $|0E\rangle$ represents the pair of E states, with the θ member of the pair coming first, and

$$\mu^{\mathrm{ii}}=V_T{}^S(0T_1\|T_2\|1T_1)/E(1T_1)\,,\qquad \mu^{\mathrm{iii}}=V_T{}^S(0T_1\|T_2\|0T_2)/E(0T_2)\,,\qquad (4.13)$$
$$\mu^{\mathrm{iv}}=V_T{}^S(0T_1\|T_2\|0A_2)/E(0A_2)\,,\qquad \mu^{\mathrm{v}}=V_T{}^S(0T_1\|T_2\|0E)/E(0E)\,.$$

V. *g* VALUES IN THE GROUND STATE

In this strong Jahn-Teller coupling approximation the electronic part of the ground states is an orbital singlet, so the expectation value of the angular momentum is identically zero, and the g values are those appropriate to a free spin. But we also know that in ions with orbital singlet ground states we expect there to be orbital effects on the g values through spin-orbit coupling to excited states, and it can be expressed, in the formalism due to Abragam and Pryce[9] as follows: We take as our Hamiltonian

$$\mathcal{H}=\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})+\lambda\mathbf{L}\cdot\mathbf{S}. \qquad (5.1)$$

The spin-orbit coupling term is large compared with the rest, but has no effect within the ground state, so we take $\beta\mathbf{H}\cdot\mathbf{L}+\lambda\mathbf{L}\cdot\mathbf{S}$ to second order, keeping the terms that are linear in λ. This gives us

$$\mathcal{H}=2\beta\mathbf{H}\cdot\mathbf{S}-\sum_{n,i,j}\frac{L_i|n\rangle\langle n|L_j}{E_n}\beta\lambda(H_iS_j+H_jS_i)\,, \qquad (5.2)$$

where the suffixes i and j label components of a vector, and $|n\rangle$ is an excited orbital state with energy E_n.

In our problem there are two excited states that couple to the ground state via the angular momentum operator; these are the states deriving from the other two roots of the Hamiltonian (2.1). (In a practical problem there may well be other states so coupled, but here we are only discussing effects within the orbital triplet.) We shall assume that they are degenerate, with $E_n=\frac{3}{2}E_{JT}$; this is true at the trigonal and tetragonal turning points in phase space and at every point on the equipotential surface when the trigonal and tetragonal energies are equal, so it is as good as most other assumptions in this model. We shall assume that the adiabatic approximation holds, so that we first find orbital angular momentum matrix elements for a fixed set of normal-mode coordinates, and then average the result over the ground vibronic state. We need to find

$$\langle L_iL_j\rangle=\langle 1|L_i|2\rangle\langle 2|L_j|1\rangle+\langle 1|L_i|3\rangle\langle 3|L_j|1\rangle\,, \qquad (5.3)$$

where

$$|1\rangle=\sin\theta\,\cos\phi|\xi\rangle+\sin\theta\,\sin\phi|\eta\rangle+\cos\theta|\zeta\rangle$$

in the notation of previous sections, and $|2\rangle$ and $|3\rangle$ are two linear combinations of $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ orthogonal to $|1\rangle$. Let us write them as

$$\begin{aligned}|1\rangle&=l_{11}|\xi\rangle+l_{12}|\eta\rangle+l_{13}|\zeta\rangle\,,\\ |2\rangle&=l_{21}|\xi\rangle+l_{22}|\eta\rangle+l_{23}|\zeta\rangle\,,\\ |3\rangle&=l_{31}|\xi\rangle+l_{32}|\eta\rangle+l_{33}|\zeta\rangle\,,\end{aligned} \qquad (5.4)$$

where the l's are elements of an orthogonal matrix. Then, for instance,

$$\langle 1|L_z|2\rangle=(l_{11}l_{22}-l_{21}l_{12})\langle\xi|L_z|\eta\rangle=il_{33} \qquad (5.5)$$

since $\langle\xi|L_z|\eta\rangle=i$ and $L_z|\zeta\rangle=0$, and similarly for other matrix elements. Using these, we find

$$\begin{aligned}\langle L_zL_z\rangle&=1-\cos^2\theta\,,\\ \langle L_xL_x\rangle&=1-\sin^2\theta\,\cos^2\phi\,,\\ \langle L_yL_y\rangle&=1-\sin^2\theta\,\sin^2\phi\,,\\ \langle L_xL_y\rangle&=\langle L_yL_x\rangle=-\sin^2\theta\,\cos\phi\,\sin\phi\,,\\ \langle L_yL_z\rangle&=\langle L_zL_y\rangle=-\sin\theta\,\cos\theta\,\sin\phi\,,\\ \langle L_zL_x\rangle&=\langle L_xL_z\rangle=-\sin\theta\,\cos\theta\,\cos\phi.\end{aligned} \qquad (5.6)$$

Comparison with the expressions (3.6) and (3.7) shows that if we now take expectation values of these operators in the ground vibronic state, we get

$$\begin{aligned}\langle L_zL_z\rangle_0&=\tfrac{2}{3}\iota+\tfrac{2}{3}K(E)\epsilon_\theta\,,\\ \langle L_xL_x\rangle_0&=\tfrac{2}{3}\iota+K(E)\tfrac{1}{3}(-\epsilon_\theta+\sqrt{3}\epsilon_\epsilon)\,,\\ \langle L_yL_y\rangle_0&=\tfrac{2}{3}\iota+K(E)\tfrac{1}{3}(-\epsilon_\theta-\sqrt{3}\epsilon_\epsilon)\,,\\ \langle L_xL_y\rangle_0&=\langle L_yL_x\rangle_0=\tfrac{1}{2}K(T_2)\tau_\zeta\,,\\ \langle L_yL_z\rangle_0&=\langle L_zL_y\rangle_0=\tfrac{1}{2}K(T_2)\tau_\xi\,,\\ \langle L_zL_x\rangle_0&=\langle L_xL_z\rangle_0=\tfrac{1}{2}K(T_2)\tau_\eta.\end{aligned} \qquad (5.7)$$

When these are substituted into the spin Hamiltonian (5.2) we get an expression of the form

$$\begin{aligned}\mathcal{H}_Z=&(2-\tfrac{2}{3}\delta)\iota\beta\mathbf{S}\cdot\mathbf{H}-\beta\delta K(E)\\ &\times[(S_zH_z-\tfrac{1}{3}\mathbf{S}\cdot\mathbf{H})\epsilon_\theta+\sqrt{3}^{-1}(S_xH_x-S_yH_y)\epsilon_\epsilon]\\ &-\beta\delta K(T_2)[\tfrac{1}{2}(S_yH_z+S_zH_y)\tau_\xi\\ &\quad+\tfrac{1}{2}(S_zH_x+S_xH_z)\tau_\eta+\tfrac{1}{2}(S_xH_y+S_yH_x)\tau_\zeta]\,,\end{aligned} \qquad (5.8)$$

where $\mathcal{H}_Z$ operates in the ground vibronic triplet and the spin states, and $\delta=\lambda/\frac{3}{2}E_{JT}$. This form of the spin Hamiltonian, if $K(E)$, $K(T_2)$, and δ are taken as parameters, is the most general form bilinear and symmetric in $\mathbf{S}$ and $\mathbf{H}$ under cubic symmetry, and so should be rather generally valid.

Finding the eigenvalues of this spin Hamiltonian is made very much simpler by the fact that $\delta\ll 2$ (this must be so if our model is valid). This means that the isotropic part of the spin Hamiltonian is dominant, and

---

[9] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

to a good approximation the spin is quantized along the direction of the magnetic field, so that if we transform to axes along and perpendicular to the field, the perpendicular spin operators can be left out. If we take **H** to be in a direction with direction cosines (l_1,l_2,l_3), then H_iS_j is to be replaced by $l_il_jH_z'S_z'$, where z' is in the direction of **H**. Using this, we get the spin Hamiltonian in the form

$$\begin{aligned}\mathcal{H}/\beta = {} & (2-\tfrac{2}{3}\delta)\iota S_z'H_z' \\ & -\delta K(E)[(l_3^2-\tfrac{1}{3})\epsilon_\theta+\sqrt{3}^{-1}(l_1^2-l_2^2)\epsilon_\epsilon]S_z'H_z' \\ & -\delta K(T_2)[l_2l_3\tau_\xi+l_3l_1\tau_\eta+l_1l_2\tau_\zeta]S_z'H_z'. \qquad (5.9)\end{aligned}$$

Note that this is still a 3×3 matrix. The roots of this matrix, which will of course depend on (l_1,l_2,l_3), give three different coefficients of $S_z'H_z'$, which will be the g values for the three transitions observed with the field in this particular direction.

Since we are looking for the roots of a cubic equation, it is not possible to write down an explicit expression for the angular dependence for general values of $K(E)$ and $K(T_2)$, though the roots can, of course, be found for any particular values of the parameters. Another reason for not trying to write down any kind of general angular dependence is that the effect of random local strains in the crystal will probably alter the form of the spin Hamiltonian, as we shall see later. There are however some values of the parameters for which explicit angular dependences can be found easily. One of these, as we might expect, is when $K(E)=K(T_2)$, i.e., when the trigonal and tetragonal Jahn-Teller energies are equal. In this case we get

$$\frac{\mathcal{H}}{\beta}=(2-\tfrac{2}{3}\delta)\iota S_z'H_z'-\delta K(E) \times\begin{bmatrix}-l_1^2+\frac{1}{3} & -l_1l_2 & -l_1l_3 \\ -l_1l_2 & -l_2^2+\frac{1}{3} & -l_2l_3 \\ -l_1l_3 & -l_2l_3 & -l_3^2+\frac{1}{3}\end{bmatrix} S_z'H_z', \qquad (5.10)$$

when the roots of the matrix are $+\frac{1}{3}+\frac{1}{3}-\frac{2}{3}$, independent of the direction cosines. Consequently, we should expect to see in this case a completely isotropic spectrum with two transitions at $g=2-[\frac{2}{3}+\frac{1}{3}K(E)]\delta$ and one at $g=2-[\frac{2}{3}-\frac{2}{3}K(E)]\delta$. A second special case occurs when $K(E)\gg K(T_2)$, i.e., when the tetragonal distortions are favored. Then we find

$$\frac{\mathcal{H}}{\beta}=(2-\tfrac{2}{3}\delta)\iota S_z'H_z'-\delta K(E) +\begin{bmatrix}-l_1^2+\frac{1}{3} & 0 & 0 \\ 0 & -l_2^2+\frac{1}{3} & 0 \\ 0 & 0 & -l_3^2+\frac{1}{3}\end{bmatrix} S_z'H_z'. \qquad (5.11)$$

The spectrum will be just the same as that of an assembly of ions each with

$$\begin{aligned} g_{\shortparallel}&=2-[\tfrac{2}{3}-\tfrac{2}{3}K(E)]\delta, \qquad (5.12)\\ g_{\perp}&=2-[\tfrac{2}{3}+\tfrac{1}{3}K(E)]\delta,\end{aligned}$$

and with their principal axes distributed among the cubic axes of the crystal. The opposite state of affairs $K(T_2)\gg K(E)$ is more complicated because the approach of the A_2 vibronic singlet to the ground triplet should also be taken into account. We shall not pursue that problem here.

It has been pointed out by Ham[10] and by Williams *et al.*[11] that the term in the Hamiltonian that determines the eigenstates in a magnetic field, being of order $\delta\beta H$, may very likely be small compared with the effect of small local strains which may be expected to be present in the crystal. This means that we should put in the effect of strains first, and then consider the effect of the magnetic field on these strain stabilized states. The result is particularly simple if we suppose the E-type strain predominates, either because of the details of the crystal structure or because $K(E)\gg K(T_2)$. The three states that are stabilized by this strain are just the three states in terms of which our matrices have been set up. The result is that we can ignore off-diagonal matrix elements. Again, the set of g values is that appropriate to a collection of ions with axial symmetry about the crystal axes (even though the actual linear combination of E-type strains may correspond to a local symmetry that is lower than axial). The effect of T_2-type strains, or a combination of both types, could also be calculated, as could the result of strain and magnetic field effects being comparable in size. Either of these situations would be liable to produce an unusual dependence of the spectrum on the direction of the field.

If the effect of small local strains is large enough to stabilize the states against mixing by a magnetic field, the effect of large externally applied strains should also do so, but as we saw in Sec. IV we may also have to consider their effect in mixing in excited vibronic states. The ground states produced by a general strain are given in Eqs. (4.10) and (4.11). We can now calculate the g values for this set of states. First, we rewrite the spin Hamiltonian (5.9) in operator form, to allow it to operate on the states mixed into the ground state. It becomes, in an obvious notation,

$$\begin{aligned}\mathcal{H}/\beta = {} & (2-\tfrac{2}{3}\delta)IS_z'H_z'-\delta \\ & \times[(l_3^2-\tfrac{1}{3})E_\theta+\sqrt{3}^{-1}(l_1^2-l_2^2)E_\epsilon]S_z'H_z' \\ & -\delta(l_2l_3T_{2\xi}+l_3l_1T_{2\eta}+l_1l_2T_{2\zeta})S_z'H_z'. \qquad (5.13)\end{aligned}$$

Now the admixtures to the ground state will be small, so their largest g-value contribution will be in cross terms between the admixtures and the original ground states, giving rise to changes in g linear in the strains. Operating with (5.13), using (4.10) and (4.11) to give

---

[10] F. S. Ham. Phys. Rev. **166**, 307 (1968).

[11] F. I. B. Williams, D. C. Krupka, and D. P. Breen, Phys. Rev. **179**, 255 (1969).

the admixtures, and picking out just these linear terms, we find changes in the g matrix given by

$$\begin{aligned}\Delta g/2\delta = {} & [\mu(e_\theta\epsilon_\theta+e_\epsilon\epsilon_\epsilon)+\mu^{\mathrm{ii}}(e_\xi\tau_\xi+e_\eta\tau_\eta+e_\zeta\tau_\zeta)]\{(0T_1\|E\|1T_1)[(l_3^2-\tfrac{1}{3})\epsilon_\theta+\sqrt{3}^{-1}(l_1^2-l_2^2)\epsilon_\epsilon] \\ & +(0T_1\|T_2\|1T_1)[l_2l_3\tau_\xi+l_3l_1\tau_\eta+l_1l_2\tau_\zeta]\}+[\mu^{\mathrm{i}}(e_\theta\epsilon_\epsilon-e_\epsilon\epsilon_\theta)+\mu^{\mathrm{iii}}(e_\xi\gamma_\xi+e_\eta\gamma_\eta+e_\zeta\gamma_\zeta)] \\ & \times\{(0T_1\|E\|0T_2)[(l_3^2-\tfrac{1}{3})\epsilon_\epsilon-\sqrt{3}^{-1}(l_1^2-l_2^2)\epsilon_\theta]+(0T_1\|T_2\|0T_2)[l_2l_3\tilde{\gamma}_\xi+l_3l_1\tilde{\gamma}_\eta+l_1l_2\tilde{\gamma}_\zeta]\} \\ & +\mu^{\mathrm{iv}}(e_\xi\alpha_\xi+e_\eta\alpha_\eta+e_\zeta\alpha_\zeta)(0T_1\|T_2\|0A_2)(l_2l_3\tilde{\alpha}_\xi+l_3l_1\tilde{\alpha}_\eta+l_1l_2\tilde{\alpha}_\zeta) \\ & +\mu^{\mathrm{v}}(e_\xi\beta_\xi+e_\eta\beta_\eta+e_\zeta\beta_\zeta)(0T_1\|T_2\|0E)(l_2l_3\tilde{\beta}_\xi+l_3l_1\tilde{\beta}_\eta+l_1l_2\tilde{\beta}_\zeta). \qquad (5.14)\end{aligned}$$

(Here a tilde has been used to indicate a transposed matrix.) This whole expression for Δg, now a 3×3 matrix which must be added to (5.9), the 3×3 matrix expression for g, is to be diagonalized to give the observed g values with the field in a direction (l_1,l_2,l_3) and a given set of strains produced by external forces. As with the original g matrix, this one can be simplified if we are justified in assuming that the effect of local and applied strains is sufficient to override off-diagonal terms in it. Thus, we now have to pick out just the diagonal terms in (5.14). Inspection of the various matrices shows that these terms are given by the expression

$$\begin{aligned}\Delta g/2\delta = {} & \mu(e_\theta\epsilon_\theta+e_\epsilon\epsilon_\epsilon)(0T_1\|E\|1T_1)[(l_3^2-\tfrac{1}{3})\epsilon_\theta+\sqrt{3}^{-1}(l_1^2-l_2^2)\epsilon_\epsilon] \\ & +\mu^{\mathrm{i}}(e_\theta\epsilon_\epsilon-e_\epsilon\epsilon_\theta)(0T_1\|E\|0T_2)[(l_3^2-\tfrac{1}{3})\epsilon_\epsilon-\sqrt{3}^{-1}(l_1^2-l_2^2)\epsilon_\theta] \\ & +\mu^{\mathrm{ii}}(0T_1\|T_2\|1T_1)(e_\xi l_2l_3\tau_\xi\tau_\xi+e_\eta l_3l_1\tau_\eta\tau_\eta+e_\zeta l_1l_2\tau_\zeta\tau_\zeta) \\ & +\mu^{\mathrm{iii}}(0T_1\|T_2\|0T_2)(e_\xi l_2l_3\gamma_\xi\tilde{\gamma}_\xi+e_\eta l_3l_1\gamma_\eta\tilde{\gamma}_\eta+e_\zeta l_1l_2\gamma_\zeta\tilde{\gamma}_\zeta) \\ & +\mu^{\mathrm{iv}}(0T_1\|T_2\|0A_2)(e_\xi l_2l_3\alpha_\xi\tilde{\alpha}_\xi+e_\eta l_3l_1\alpha_\eta\tilde{\alpha}_\eta+e_\zeta l_1l_2\alpha_\zeta\tilde{\alpha}_\zeta) \\ & +\mu^{\mathrm{v}}(0T_1\|T_2\|0E)(e_\xi l_2l_3\beta_\xi\tilde{\beta}_\xi+e_\eta l_3l_1\beta_\eta\tilde{\beta}_\eta+e_\zeta l_1l_2\beta_\zeta\tilde{\beta}_\zeta). \qquad (5.15)\end{aligned}$$

It is interesting that this expression can be rewritten to show that the parameters it contains are sufficient to account for all the parameters in the tensor relation between **S**, **H** and e under *tetragonal* symmetry, except that any effect of a totally symmetric strain is missing, as are the terms corresponding to an equal shift of all the g values. Such terms would arise from effects outside the scope of this model. If $K(T_2)$ in the ground state is not vanishingly small, and the applied stress is such as to produce T_2-type strains, then the form (5.14) must be retained for the strain-dependent part of g, and we should not expect **S**, **H**, and e to have a simple tensor relationship.

VI. EFFECT OF COUPLING TO MANY MODES

Generally in a crystal the Jahn-Teller coupling is not to a single mode of vibration of each symmetry, but to a large number of such modes. This can be expressed by modifying the Hamiltonian (2.1) to read

$$\begin{aligned}\mathcal{H} = {} & \sum_i V_E{}^i(Q_\theta{}^i\epsilon_\theta+Q_\epsilon{}^i\epsilon_\epsilon) \\ & +\sum_j V_T{}^j(Q_\xi{}^j\tau_\xi+Q_\eta{}^j\tau_\eta+Q_\zeta{}^j\tau_\zeta)+\mathcal{H}_{0t}, \\ \mathcal{H}_0 = {} & \sum_i \frac{1}{2\mu_E{}^i}\{(P_\theta{}^i)^2+(P_\epsilon{}^i)^2 \\ & +(\mu_E{}^i)^2(\omega_E{}^i)^2[(Q_\theta{}^i)^2+(Q_\epsilon{}^i)^2]\} \qquad (6.1) \\ & +\sum_j \frac{1}{2\mu_T{}^j}\{(P_\xi{}^j)^2+(P_\eta{}^j)^2+(P_\zeta{}^j)^2 \\ & +(\mu_T{}^j)^2(\omega_T{}^j)^2[(Q_\xi{}^j)^2+(Q_\eta{}^j)^2+(Q_\zeta{}^j)^2]\},\end{aligned}$$

where the sum is over all normal modes of the appropriate symmetry.

Using this Hamiltonian instead of (2.1), the analysis of Öpik and Pryce[6] shows that there are still only the same two kinds of minimum in the potential, and the values of the parameters are those shown in Table II.

Note that although there are many more degrees of freedom than before, the number and kind of the minima in the potential energy are unaltered. There are still just three tetragonal and four trigonal distortions that correspond to turning points in the potential energy out of the large number of possible trigonal and tetragonal distortions.

If the energies of the trigonal and tetragonal turning points happen to be equal, then as before, we find that there is a two-dimensional surface in the many-dimensional Q space on which the potential energy is constant and lower than anywhere else. This surface can be parametrized in terms of the angles θ and ϕ as before, and it is given by the set of equations

$$\begin{aligned}Q_\theta{}^i &= [V_E{}^i/\mu_E{}^i(\omega_E{}^i)^2]\tfrac{1}{2}(3\cos^2\theta-1), \\ Q_\epsilon{}^i &= [V_E{}^i/\mu_E{}^i(\omega_E{}^i)^2]\tfrac{1}{2}\sqrt{3}\sin^2\theta\cos2\phi, \\ Q_\xi{}^j &= [V_T{}^j/\mu_T{}^j(\omega_T{}^j)^2]\sin2\theta\sin\phi, \qquad (6.2) \\ Q_\eta{}^j &= [V_T{}^j/\mu_T{}^j(\omega_T{}^j)^2]\sin2\theta\cos\phi, \\ Q_\zeta{}^j &= [V_T{}^j/\mu_T{}^j(\omega_T{}^j)^2]\sin^2\theta\sin2\phi.\end{aligned}$$

If we assume as before that the lowest-energy levels will be those in which the representative point in Q space is constrained to move on this surface and look for an expression for the kinetic energy in terms of θ and ϕ only, we find the same simple form (2.21) as before if

$$\sum_i \frac{(V_E{}^i)^2}{\mu_E{}^i(\omega_E{}^i)^4}=\frac{4}{3}\sum_j \frac{(V_T{}^j)^2}{\mu_T{}^j(\omega_T{}^j)^4} \qquad (6.3)$$

TABLE II. Values of the normal coordinates at the two possible types of minima in the potential energy. The notation is as in Table I.

	1	2
Q_θ^k	$-V_E^k e_{i\theta}/\mu_E^k(\omega_E^k)^2$	0
Q_ϵ^k	$-V_E^k e_{i\epsilon}/\mu_E^k(\omega_E^k)^2$	0
Q_ξ^j	0	$[2V_T^j/3\mu_T^j(\omega_T^j)^2]m_1$
Q_η^j	0	$[2V_T^j/3\mu_T^j(\omega_T^j)^2]m_2$
Q_ζ^j	0	$[2V_T^j/3\mu_T^j(\omega_T^j)^2]m_3$
E_{JT}	$\frac{1}{2}\sum_k \frac{(V_E^k)^2}{\mu_E^k(\omega_E^k)^2}$	$\frac{2}{3}\sum_j \frac{(V_T^j)^2}{\mu_T^j(\omega_T^j)^2}$

and ω^2/q^2 in (2.21) is replaced by

$$\left(\sum_i \frac{(V_E^i)^2}{\mu_E^i(\omega_E^i)^4}\right)^{-1}.$$

This condition (6.3) reduces, when only one mode of each kind is included in the sum, to our original condition $\omega_E = \omega_T$. Small differences from equality in Eq. (6.3) can be transformed into small differences between the trigonal and tetragonal energies just as in the single-mode case.

Thus, we see that if the appropriate conditions are satisfied, the lowest-energy levels are given by solutions of the θ, ϕ Schrödinger equation (3.4) as before. However, there does arise an extra complication in connection with the validity of the approximation, i.e., in order to assume that the system is in the ground state of all those parts of the Hamiltonian corresponding to motion away from the θ, ϕ surface, we must have the characteristic splitting of the θ, ϕ energy levels small compared with $\hbar\omega$ (2.25). That is to say, we require

$$\hbar^2\left(\sum_i \frac{(V_E^i)^2}{\mu_E^i(\omega_E^i)^4}\right)^{-1} \ll \hbar\omega_E^j,\ \hbar\omega_T^j \tag{6.4}$$

for all of the frequencies ω_E^j, ω_T^j. This is obviously impossible if all the normal modes of vibration of the crystal are included, since their frequencies go right down to zero. However, it is reasonable to assume that the Jahn-Teller coupling to these very long-wavelength modes is rather small, so that we might initially neglect all the modes below a certain frequency, and introduce them subsequently as a perturbation. These low-frequency modes, weakly coupled, will introduce a relaxation mechanism and broaden the energy levels in the excited states. Thus, while we should expect to find a ground state with rather the same properties as the single mode case, we should expect the excited states to be considerably spread out by the coupling to many modes.

VII. RELAXATION PROCESSES

If the ground eigenstates are stabilized by local or externally produced strains, we must ask how the system can relax from one of these states to another. This will happen by coupling to the thermal lattice vibrations, either by a "direct" process from one component of the ground state to another, or by an "indirect" process of excitation to an excited vibronic state and back. The indirect process would be characterized by a temperature dependence of the $e^{-E/kT}$ kind, where E is the energy of the excited vibronic state. The usual method of calculating such processes analyzes the thermal phonons in terms of strains, and considers the effect of such time-dependent strains in producing transitions between the localized states.

It is obvious that when we come to apply that method here it is no good to look at E-type strains, which are diagonal in the ground state, and if exciting transitions to excited T_1 and T_2 vibronic states, could only return the system to the same ground-state component that it started from, at least in this approximation. On the other hand, T_2-type strains do have off-diagonal matrix elements that may be active in direct or indirect processes. For direct processes we need matrix elements of T_2-type strains within the ground triplet. Since, as we have seen, these are proportional to $K(T_2)$, if the system has overridingly strong tetragonal coupling with $K(T_2)$ vanishingly small, then such direct processes can be neglected. However, in the intermediate region where $K(T_2)$, though small, does not vanish, the direct processes are possible and will be the dominant relaxation processes at low temperatures. For indirect processes, as we saw in Sec. IV, a T_2-type strain has many off-diagonal matrix elements to excited vibronic states, and some of these are sure to be nonzero. Thus we should always expect to find effective indirect processes, which may be expected to be dominant at higher temperatures.

It should be emphasized that we are now talking about a situation in which the Hamiltonian no longer has perfect cubic symmetry. The ground triplet is split by distortions of the surroundings associated with local or externally produced strains. We consider the ways in which transitions can be induced between the components of the triplet. If the Hamiltonian remains cubic the triplet state is strictly degenerate, and no splitting can be produced by tunneling or other relaxation processes.

VIII. EXPERIMENTAL APPLICATIONS

Most examples of a strong Jahn-Teller effect in a triplet state have been interpreted in terms of strong coupling to one type of mode and small coupling to the other, which usually suffices to explain the experimental results. The work presented here goes some way to explain why this assumption of extreme imbalance between the modes should work so well. However, some systems are known in which it does not work.

One such system, for which this calculation would seem to offer an explanation, is the F center in calcium oxide. In this center the orbital triplet is an excited state, while the ground state is an orbital singlet, and the properties of the singlet-triplet absorption spectrum are studied. The spectrum consists of a broad band together with a sharp zero-phonon line. Both are supposedly associated with the F center, though some doubt still exists about this. Faraday rotation measurements on both broad and sharp lines have been reported by Kemp *et al.*[12] and by Bessent *et al.*,[13] and stress and Zeeman-effect measurements on the sharp line by Hughes and Runciman.[14] The evidence from magnetic measurements on the sharp line implies that spin-orbit coupling is almost completely quenched, while under stress the line splits as if there was coupling to both E_g and T_{2g} distortions. The quenching of the spin-orbit coupling suggests that the Jahn-Teller coupling is strong. The existence of coupling to both E_g and T_{2g} strains requires that neither $K(E)$ nor $K\ (T_2)$ be zero. In terms of the model used in this paper the ground or zero-phonon state in the orbital triplet should therefore correspond to a situation in the dynamical regime near $\Delta=0$; the experimental results could not be explained by coupling to either mode alone.

A problem that does not seem to be any further resolved by this work is that of the ground vibronic state of the excited orbital triplet of V^{++} in MgO. Sturge[15] discussed measurements he made on the effect of stress on the zero-phonon line in the singlet-triplet transition. He proposed an interpretation in terms of an effective Hamiltonian incorporating the effect of a distribution of static trigonal distortions. Ham[16] showed that the results could also be explained if the ground state consisted not of a single T_2 state, but also of T_2 and T_1 states nearly degenerate, with another T_2 state about 40 cm^{-1} up. A look at Fig. 2 shows that this condition is not even approximately satisfied anywhere on it (in V^{++} the orbital triplet is a T_2 one, so 1 and 2 should be interchanged on the figure for this ion). Also, Ham's explanation requires that both the T_2 states be equally narrow. On our model, relaxation and coupling to many modes would probably broaden the higher states considerably.

The work of Watkins[17] on the positively-charged vacancy in Si presents another possible application. In this center the ground state is an orbital triplet with a spin of one-half, and the spin-resonance spectrum is that appropriate to the three tetragonal distortions, indicating that Δ is large and negative. However, relaxation studies indicate that the effective-energy barrier between the tetragonal distortions is rather small compared with the Jahn-Teller energy. If we assume that this barrier represents the height of the saddle points in the Öpik-Pryce[6] calculation, this implies also that Δ is small compared with the Jahn-Teller energy, and the coupling to T_2 modes of vibration should not be entirely neglected. We have tried to describe this center in terms of the parameters that emerge from this theory, and in particular to account for the effects of stress in altering the g values. The results have been inconclusive so far, and are not worth further discussion here.

ACKNOWLEDGMENTS

This work was begun at the General Electric Research and Development Center and was continued in the Department of Engineering and Applied Science at Yale University. I am very grateful to both institutions for their support and provision of computing facilities. I also thank the National Science Foundation for a Senior Visiting Scientist Fellowship. I am grateful for all the help and suggestions I have received throughout from F. S. Ham and G. D. Watkins. I also wish to thank W. M. Schwarz and G. M. Copland for their advice on computing and the provision of programs.

---

[12] J. C. Kemp, W. M. Ziniker, J. A. Glaze, and J. C. Cheng, Phys. Rev. **171**, 1024 (1968).

[13] R. G. Bessent, B. C. Cavenett, and I. C. Hunter, J. Phys. Chem. Solids **29**, 1523 (1968).

[14] A. E. Hughes and W. A. Runciman, J. Phys. **C2**, 37 (1969).

[15] M. D. Sturge, Phys. Rev. **140**, A880 (1965).

[16] F. S. Ham, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Wiley-Interscience, Inc., New York, 1967), p. 357.

[17] G. D. Watkins, J. Phys. Soc. Japan **18**, Suppl. II, 22 (1963).